

# SCIENCE FOR CERAMIC PRODUCTION

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## PRODUCTION OF SILICON CARBIDE BASED MATERIALS BY LIQUID-PHASE SINTERING (REVIEW)

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The possibility of obtaining silicon carbide based ceramic by liquid-phase sintering with modification by eutectic additives is examined. It is shown that the samples synthesized are similar to silicon carbide samples obtained by reaction sintering, but they surpass the latter in terms of energy efficiency.

**Key words:** silicon carbide, eutectic, energy efficiency, sintering temperature, mechanical strength.

The concepts for transforming Russian industry are based on the creation of technologies for fundamentally new materials that make it possible to develop new sectors of the economy. The latter applies fully to ceramics, metals, polymers and glass; it also touches upon composite materials that can be produced on their basis.

Looking at ceramic materials science it becomes evident that ceramic materials are characterized by unique physical and technical properties which no one class of materials possesses. Construction ceramic displaces a number of metals and alloys used for similar purposes. The average yearly increase in the production of construction ceramic in the USA in 2002–2008 was 11.8% in terms of cost. Ceramics, containing mainly SiC, Si<sub>3</sub>N<sub>4</sub>, Al<sub>2</sub>O<sub>3</sub> and ZrO<sub>2</sub> now account for more than 20% of the world production of construction materials, and their role will increase in the future, in several decades equaling and possibly even surpassing the contribution of metals to the production of construction materials [1–3].

New approaches to the technology of synthesizing strengthening components, the principles for picking and types of sintering additives, as well as improving methods for preparing powders and heat-treatment regimes make it possible to significantly improving the physical and chemical properties of silicon carbide materials.

There is a real need to create a fundamentally new methodology for developing modern ceramic materials that is

based, on the one hand, on new approaches to picking modifying components (sintering, strengthening and others) and, on the other hand, on improving existing technological principles at all stages of the development of a material that would make it possible in fabricating specific articles to realize to the maximum extent possible the unique properties of the chemical compounds comprising a ceramic material. Therefore, conceptually, designing new-generation materials must be viewed from the standpoints of the interrelations and mutual influence in the system composition – structure – property – technology. This approach is general and can be implemented in creating construction and durable SiC-based composite materials.

Undoubtedly, there are diverse ways for solving these problems in application to specific operating regimes of parts. Nonetheless, the basis for them is an understanding of the physical and chemical processes occurring at all stages of ceramic material design, specifically, during grinding (gives rise to mechanical-chemical activation), molding (responsible for the formation of the primary structure) and firing (makes it possible to realize the microstructure of the ceramic). These technological stages are the fundamental stages in the design process and are responsible for all the properties of the materials and articles.

In the formation of microstructure (the main problem in the case at hand is to attain the maximum density and a fine-crystalline structure) it is not so much the methods of dispersion that merit special attention but rather the methods of condensation (such as the processes at the nanolevel — sol-gel process, heterophase precipitation and others), mak-

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ing it possible to obtain narrowly fractionated, spherical, micro- and nano-size powders. The latter is especially important, because according to the Gibbs–Helmholtz equation the maximum contribution to the excess surface energy of the system increases considerably as particle size decreases.

In summary, it must be concluded that the main concept in designing materials with fundamentally new properties involves the following:

- a systematic holistic approach to studying the processes responsible for the formation of the structure and properties of a ceramic material;
- establishing the interrelations in the series composition – structure – properties – technology;
- combining fundamentally new approaches to picking modifying components on the one hand and improving the existing technological principles at all stages of the development of a material on the other.

Silicon carbide is one of the most promising oxygen-free refractory compounds for obtaining construction materials for use at high temperatures. This is explained by a complex of properties which are characteristic for this compound: high melting temperature, hardness and thermal and corrosion-erosion resistance in combination with very low density compared with metals and alloys based on them ( $3.20 \text{ g/cm}^3$ ).

The principles of directly creating related structures where the crystalline phases comprising the ceramic have identical structural characteristics form the basis of the technology for obtaining high-strength materials. To secure high strength it is necessary to realize dense intergrowth of crystals in the absence of porosity, which requires high-temperature firing. The extreme energy-intensiveness of these processes makes it necessary to find new methods of controlling the formation of microstructure by using additives to decrease the sintering temperatures while maintaining high strength.

Immediately after melting a substance comprises a collection of irregular formations in dynamic equilibrium as well as regions with regular structural cybotactic groups. Thus, a melt is micro-nonuniform. Cybotactic groups can move in space and form structural combinations whose lifetime depends on the intensity of the thermal motion and the bond strength.

The structure and properties of melt depend mainly on its composition and are determined by the character of the interaction between acidic and basic elements. Regulation of the composition, structure and properties of the liquid makes it possible to control the processes leading to the formation of the required structure in order to obtain ceramic with prescribed properties, since the parameters of ions united into an ensemble differ strongly from the characteristics of individual ions and from the parameters of macro systems.

A promising method of controlling the formation of structure in SiC-based materials is to use as modifiers eutectic compositions (eutectic additives) because of the low melting temperatures and the presence of structured elements

in the liquid, which carry a “genetic” memory of the crystalline phases of the eutectic, with ordered fine-crystalline structure. Therefore, the mass transfer during sintering of the material can be regulated by optimizing the composition, structure and properties of the liquid phase on the basis of knowledge about the physical chemistry of the processes occurring during high-temperature treatment of materials.

The combined use of oxide eutectic additive and nano-disperse silicon-carbide powder makes it possible to create fundamentally new composite ceramic materials for use in the presence of intense external actions of different nature. Highly disperse crystallized phases of a eutectic protect SiC from oxidation, while nano-disperse silicon carbide powder imparts to a material the required strength, hardness and high thermophysical properties.

A fundamental aspect of the technology of new, composite, ceramic materials based on SiC is the use of, aside from the conventional nano-powders, oxides as starting components. The nanopowders synthesized by chemical methods are mechanically activated together with oxygen-free compounds in order to obtain a uniform mixture of powders that is highly active to sintering.

The choice of eutectic additives for creating silicon carbide based compositions is based on the results of physical-chemical calculations and experimental studies in the course of which it was established that on heating most oxides promote dissociation of oxygen-free compounds with gaseous products of the reaction being released. Silicon carbide remains stable to high temperatures in the presence of a limited number of oxides, among which are aluminum, magnesium, calcium and yttrium oxides.

A synthesized composite ceramic material is a dispersion-ordered (by nano-size particles) regular structure in which due to their affinity to silicon carbide the phases of the oxide components are adsorbed on the surface of its particles.

Such a composite ceramic makes it possible to fabricate the elements of the final form by isostatic pressing and subsequently fire them up to a high-density state. This eliminates the need for laborious mechanical working operations required for the fabrication of metallic elements followed by grinding and polishing of their working surfaces.

The information now available in the scientific and patent literature on composite ceramic materials based on refractory oxide and oxygen-free compounds belonging to different classes attests to the possibility of creating new composite materials with prescribed characteristics.

Analysis of publications concerning ceramic materials science shows that most research is focused on creating composite materials with high fracture toughness, strength, elastic modulus, thermal stability and other very important properties in order to ensure that critical ceramic articles operate reliably when subjected to forces of different nature.

Refractory ceramic materials are characterized by high hardness and elastic modulus, whose values surpass those of metals and alloys, as well as minimal values of the linear

**TABLE 1.** Composition and Theoretical Density of SiC Ceramic with Oxide Additives [12]

Composition No.	Component content, wt.%	Theoretical density $\rho_t$ , g/cm <sup>3</sup>
	$\alpha$ -SiC	$\text{Al}_2\text{O}_3$ – $\text{Y}_2\text{O}_3$ –MgO
1	95	5
2	90	10
3	85	15
4	80	20

thermal expansion coefficient (CLTE) and high melting temperatures.

The strength of a ceramic can be increased by decreasing the grain size of the main phase or by introducing a second component. A significant number of publications, including [4 – 7], are devoted to solving the problem of increasing the fracture toughness of ceramic materials by using fibers and dispersion-hardening particles of different compounds.

Dispersion-hardening particles have a number of advantages over continuous and discrete fibers, since they are not prone toward forming agglomerates or orientation, as a result of which ceramic composites become isotropic. Dispersion hardening of a silicon carbide matrix can be realized by using particles of oxygen-free and oxide fills.

Composite ceramic materials developed abroad (China, Japan, USA) on the basis of silicon carbide with additives of hardening particles of silicon carbide, zirconium diboride and boron nitride are well known. Such materials possess high mechanical characteristics: their ultimate strength in bending reaches 800 MPa, hardness 15 – 19 GPa and fracture toughness 5 – 6 MPa · m<sup>1/2</sup> [8 – 11].

The use of liquid-phase sintering additives in obtaining silicon carbide ceramics can significantly intensify the synthesis process and increase the degree of compaction of ceramic material. In liquid-phase sintering the bonding of the constituent particles of the system increases, and the wetting liquid phase increases the rate of diffusion of the components and facilitates the movement of the solid-phase particles.

In recent years many works have been devoted to the development of a technology of ceramic materials based on liquid-phase sintering of silicon carbide with the use of oxide additives. For example, the results of research on obtaining by liquid-phase sintering high-density materials based on silicon carbide at temperatures 1800 – 1900°C are presented in [12]. Mixtures of oxides in the system  $\text{Al}_2\text{O}_3$ – $\text{Y}_2\text{O}_3$ –MgO, forming a binary eutectic  $\text{MgO} \cdot \text{Al}_2\text{O}_3 \cdot 3\text{Y}_2\text{O}_3 \cdot 5\text{Al}_2\text{O}_3$  at 1775°C, were used as sintering additives. SiC powder with average particle size 0.8 μm as well as  $\text{Al}_2\text{O}_3$ ,  $\text{Y}_2\text{O}_3$  and MgO powders with average particle size 1.2, 0.8 and 0.6 μm were used. Four compositions with different concentrations of the oxides were chosen for densifying material to study the effect of oxide additives, taken in ratios ensuring that a eutectic in the ternary system  $\text{Al}_2\text{O}_3$ – $\text{Y}_2\text{O}_3$ –MgO is obtained.

**TABLE 2.** Characteristics of Eutectic Points of the System  $\text{Al}_2\text{O}_3$ – $\text{Y}_2\text{O}_3$ –MgO [12]

Quasibinary eutectic No.	Eutectic temperature, °C	Eutectic composition, mol.%		
		MgO	$\text{Y}_2\text{O}_3$	$\text{Al}_2\text{O}_3$
e8	1790	37.0	42.0	21.0
e9	1740	38.0	31.0	31.0
e10	1760	27.5	22.5	50.0
e11	1775	21.0	21.0	58.0

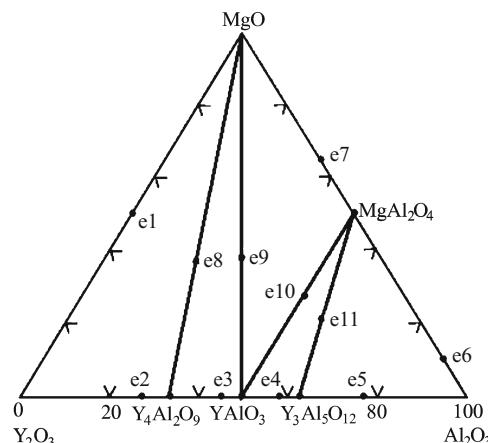
The computed densities of these materials are presented in Table 1.

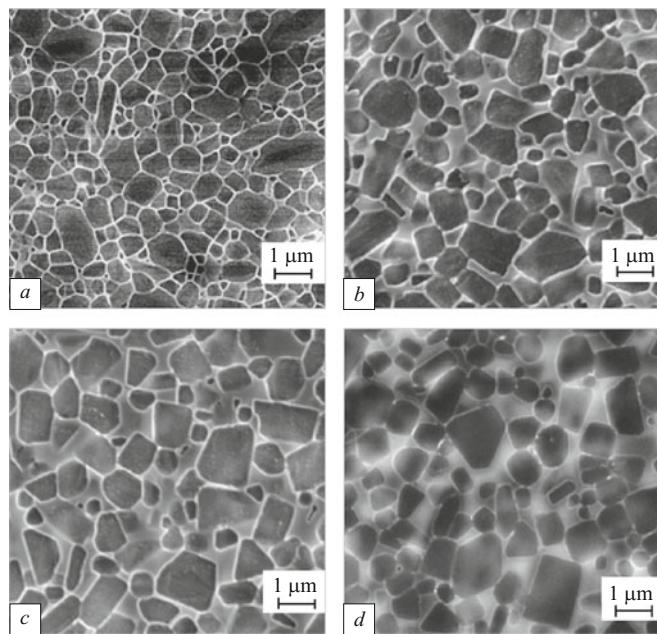
Four binary eutectic points, whose temperatures and compositions are presented in Table 2, were established in the system  $\text{Al}_2\text{O}_3$ – $\text{Y}_2\text{O}_3$ –MgO (Fig. 1) on lines of the sections between  $\text{MgO}$ – $\text{Y}_4\text{Al}_2\text{O}_9$  (e8),  $\text{MgO}$ – $\text{YAlO}_3$  (e9),  $\text{YAlO}_3$ – $\text{MgAl}_2\text{O}_4$  (e10) and  $\text{Y}_3\text{Al}_5\text{O}_{12}$ – $\text{MgAl}_2\text{O}_4$  (e11).

The samples were fired in a high-temperature vacuum furnace with graphite heaters and lining in an atmosphere consisting of ultrapure argon in the temperature internal 1800 – 1900°C with isothermal soaking for 40 min.

The structure of the material is represented by fine grains (Fig. 2) with predominately regular faceting. The authors report that the size of the solid-phase particles depends on the rate of heating, the isothermal soaking time and the amount and composition of the liquid phase.

For the minimum content of the oxide additive the silicon carbide particles are wetted by a thin layer of oxide, making impossible to optimize the liquid-phase densification process, which results in high porosity and very low mechanical characteristics. As the oxide fraction increases to 10 wt.% the amount of the liquid phase increases, which promotes active liquid-phase densification of the material and results in very small growth of silicon carbide grains. An important parameter for ceramic materials is the porosity. Its

**Fig. 1.** Phase diagram of the system (mol.%)  $\text{Al}_2\text{O}_3$ – $\text{Y}_2\text{O}_3$ –MgO [12].



**Fig. 2.** Microstructure of sintered silicon carbide materials obtained at 1860°C: a) composition 1; b) composition 2; c) composition 3; d) composition 4 (see Table 1 for composition numbers) [12].

value decreases the mechanical properties significantly (Table 3).

Research established the optimal sintering temperature of the composition  $\text{SiC}-\text{Me}(\text{Al}, \text{Mg}, \text{Y})\text{O}$  to be  $1860 \pm 10^\circ\text{C}$ , which ensures that a high-density fine-crystalline structure of the material with uniform distribution of the components is obtained [12].

The materials obtained possess high strength in bending at least  $660 \pm 15 \text{ MPa}$ , fracture toughness  $K_{\text{IC}} \geq 5.5 \pm 0.2 \text{ MPa} \cdot \text{m}^{1/2}$  and Vickers hardness  $\geq 18.5 \pm 0.3 \text{ GPa}$  [12].

The authors of [13] investigated samples with constant content of  $\text{Al}_2\text{O}_3$ ,  $\text{Y}_2\text{O}_3$  (7 and 2 wt.%, respectively) and different content of  $\text{CaO}$  (1 and 3 wt.%) as modifying additives. Sintering to relative density  $> 95\%$  was observed in the temperature interval  $1750 - 1900^\circ\text{C}$ . Compaction occurring with the participation of the liquid phase formed by  $\text{Al}_2\text{O}_3$ ,  $\text{Y}_2\text{O}_3$  and  $\text{CaO}$  resulted in the formation of fine, elongated, equiaxial grains with average size  $\leq 10 \mu\text{m}$ . The hardness, elastic modulus and fracture toughness depended on the firing temperature and microstructure. As firing temperature increased to  $1800^\circ\text{C}$  the mechanical properties increased initially and then decreased with temperature increasing to  $1900^\circ\text{C}$ . The samples fired at  $1800^\circ\text{C}$  exhibited the highest maximum fracture toughness, microhardness and elastic modulus.

The results of liquid-phase sintering of silicon carbide with  $\text{AlN}-\text{Y}_2\text{O}_3$ ,  $\text{Al}_2\text{O}_3-\text{Y}_2\text{O}_3$  and  $\text{SiO}_2-\text{Y}_2\text{O}_3$  additives are presented in [14]. The average particle size of all powders is  $0.75 \mu\text{m}$ . The total content of additives was 20 vol.%, the  $\text{Y}_2\text{O}_3$  content being 35 vol.% in each system of additives.

**TABLE 3.** Porosity and Grain Size of the Solid Phase of  $\text{SiC}$ -materials with Oxide Additive in the System  $\text{Al}_2\text{O}_3-\text{Y}_2\text{O}_3-\text{MgO}$  [12]

Composition No.	Sintering temperature, $^\circ\text{C}$	Porosity P ( $\pm 0.3$ ), %	Pore size, $\mu\text{m}$ :		Grain size $d_{\text{max}}, \mu\text{m}$
			max	min	
1	1800	12.4	2.0	0.7	1.0
	1830	8.5	1.8	0.8	1.2
	1860	6.0	2.4	0.7	2.0
	1900	9.6	4.0	1.0	2.6
2	1800	11.0	1.9	0.6	1.0
	1830	5.5	2.3	0.6	1.2
	1860	1.4	3.5	0.9	1.6
	1900	7.8	4.1	1.1	2.9
3	1800	10.0	2.3	0.5	1.1
	1830	4.3	2.5	0.6	1.5
	1860	1.0	3.1	0.9	1.8
	1900	7.0	4.2	1.0	3.2
4	1800	7.9	3.1	0.5	1.2
	1830	3.2	3.5	0.7	1.9
	1860	1.0	4.0	0.9	2.1
	1900	1.9	4.7	1.0	3.7

The samples were fired at temperatures  $1900$ ,  $2000$  and  $2100^\circ\text{C}$  in an argon atmosphere.

Much-promising results were obtained for samples based on silicon carbide with  $\text{Al}_2\text{O}_3-\text{Y}_2\text{O}_3$  additive, which were annealed at  $2000^\circ\text{C}$  and manifest the lowest mass losses (about 6 wt.%) and the highest average strength in bending — about  $433 \text{ MPa}$ . The samples with  $\text{Al}_2\text{O}_3-\text{Y}_2\text{O}_3$  and  $\text{SiO}_2-\text{Y}_2\text{O}_3$  additives showed the highest mass losses because of the reactions of  $\text{Al}_2\text{O}_3$  and  $\text{Y}_2\text{O}_3$  with the  $\text{SiC}$  matrix with formation of gaseous substances, such as  $\text{Al}_2\text{O}_3$ ,  $\text{SiO}$  and  $\text{CO}$ . As a result of these processes the liquid phase is exhausted, which degrades the density and mechanical properties.

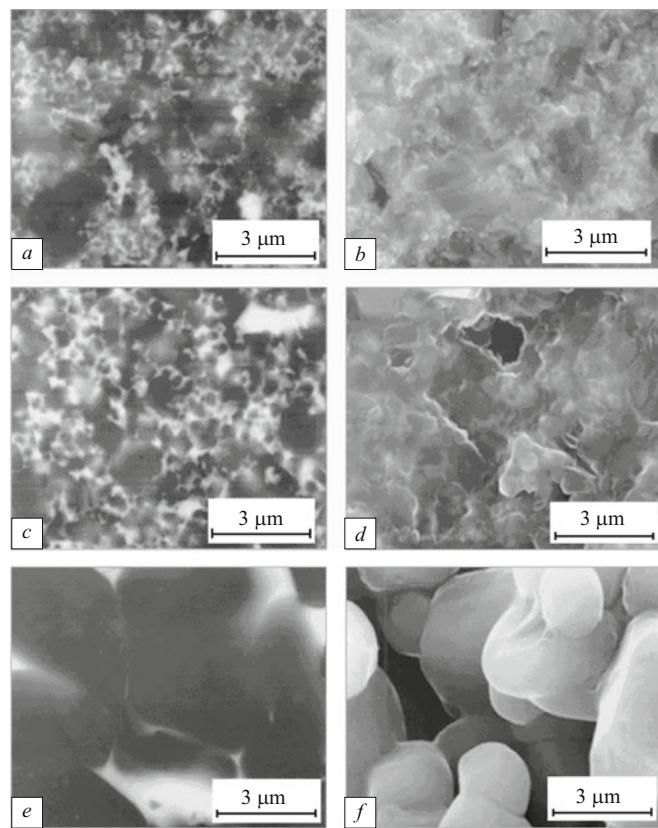
Analysis of the microstructure showed that only the  $\beta$ - $\text{SiC}$  phase is present in all samples. The phase transformations of  $\beta$ - $\text{SiC}$  and  $\alpha$ - $\text{SiC}$  are not observed (Fig. 3).

The similarity of the chemical and physical properties between the rare-earth oxides and  $\text{Y}_2\text{O}_3$  led M. Balog [5] to the idea of replacing  $\text{Y}_2\text{O}_3$  by other rare-earth oxides. This work is devoted to  $\text{SiC}$ -based ceramic obtained by modifying its mixture with rare-earth oxides ( $\text{Y}_2\text{O}_3$ ,  $\text{Yb}_2\text{O}_3$  and  $\text{Sm}_2\text{O}_3$ ) and  $\text{AlN}$ .

The compositions of the experimental samples are presented in Table 4. The samples were fabricated by hot pressing at  $1850^\circ\text{C}$  in 1 h under mechanical load  $30 \text{ MPa}$  in an  $\text{Ar} + \text{N}_2$  atmosphere and then fired at  $1900^\circ\text{C}$  in 10 h in the same atmosphere.

Relatively high values of the density were obtained. This confirms the possibility of using these additives for liquid-phase sintering of silicon carbide (Table 5).

The microstructure of the new ceramic is displayed in Figs. 4 and 5. The studies showed that firing after hot-press-



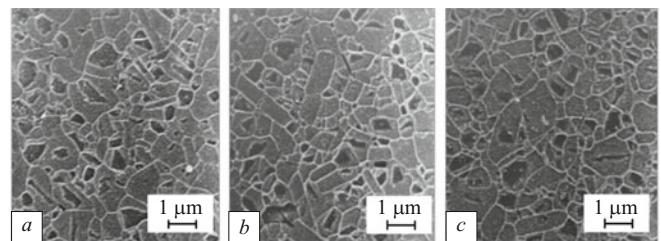
**Fig. 3.** Microstructure and cleavage surface of samples fired at 2100°C with additives AlN–Y<sub>2</sub>O<sub>3</sub> (*a, b*), Al<sub>2</sub>O<sub>3</sub>–Y<sub>2</sub>O<sub>3</sub> (*c, d*) and SiO<sub>2</sub>–Y<sub>2</sub>O<sub>3</sub> (*e, f*) [14].

ing improves the mechanical properties of ceramic. The samples with a significant content of elongated grains have a higher fracture toughness; conversely, samples with a finely disperse microstructure are characterized by higher strength.

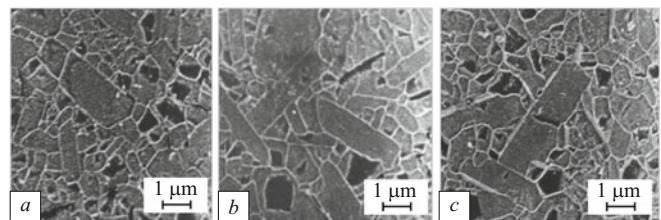
In [16] a strengthened SiC-based ceramic was obtained by hot-pressing followed by firing under pressure and using AlN and Re<sub>2</sub>O<sub>3</sub> (Re = Y<sup>3+</sup>, Yb<sup>3+</sup>) as sintering additives. The microstructure of the ceramic is represented by elongated grains of  $\alpha$ -SiC and an interstitial space in the form of a glassy phase. The strength was analyzed at high temperatures (1600°C) for silicon-carbide ceramic with additives AlN and Er<sub>2</sub>O<sub>3</sub> as well as AlN and Y<sub>2</sub>O<sub>3</sub>.  $\alpha$ -SiC,  $\beta$ -SiC, AlN, Y<sub>2</sub>O<sub>3</sub> and Yb<sub>2</sub>O<sub>3</sub> (99.9% purity) were used as initial powders; the average sizes of the  $\alpha$ -SiC and  $\beta$ -SiC particles were 0.45 and 0.27  $\mu$ m, respectively; the specific surface areas of the pow-

**TABLE 4.** Experimental Compositions [15]

Sample	Content, wt.%				
	SiC	AlN	Y <sub>2</sub> O <sub>3</sub>	Yb <sub>2</sub> O <sub>3</sub>	Sm <sub>2</sub> O <sub>3</sub>
SiC–Y <sub>2</sub> O <sub>3</sub> –Yb <sub>2</sub> O <sub>3</sub>	87	3	4.6	5.4	—
SiC–Y <sub>2</sub> O <sub>3</sub> –Sm <sub>2</sub> O <sub>3</sub>	87	3	3.9	—	6.1
SiC–Yb <sub>2</sub> O <sub>3</sub> –Sm <sub>2</sub> O <sub>3</sub>	87	3	—	5.3	4.7



**Fig. 4.** Microstructure of hot-pressed samples: *a*) SiC–Y<sub>2</sub>O<sub>3</sub>–Yb<sub>2</sub>O<sub>3</sub>; *b*) SiC–Y<sub>2</sub>O<sub>3</sub>–Sm<sub>2</sub>O<sub>3</sub>; *c*) SiC–Yb<sub>2</sub>O<sub>3</sub>–Sm<sub>2</sub>O<sub>3</sub> [15].



**Fig. 5.** Microstructure of fired samples: *a*) SiC–Y<sub>2</sub>O<sub>3</sub>; *b*) SiC–Y<sub>2</sub>O<sub>3</sub>–Sm<sub>2</sub>O<sub>3</sub>; *c*) SiC–Yb<sub>2</sub>O<sub>3</sub>–Sm<sub>2</sub>O<sub>3</sub> [15].

ders were 15 and 17.5  $\text{m}^2/\text{g}$ , respectively. The initial batch was hot-pressed at 1900°C for 1 h under pressure 25 MPa in a nitrogen atmosphere. Next, the hot-pressed materials were fired at 2000°C for 6 h under pressure 25 MPa.

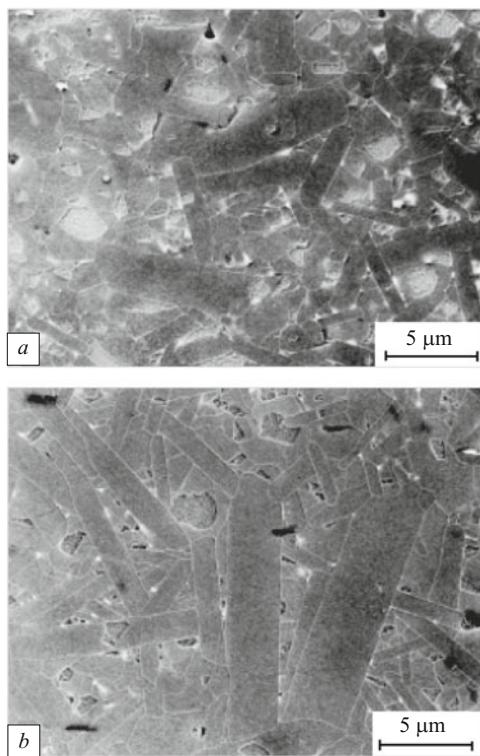
The relative densities of the synthesized materials are presented in Table 6. The hot-pressed and fired silicon carbide based ceramic with AlN and Re<sub>2</sub>O<sub>3</sub> additives is characterized by density above 98.0%. The AlN and Re<sub>2</sub>O<sub>3</sub> additives form a liquid phase with SiO<sub>2</sub>, which promotes com-

**TABLE 5.** Relative Density of Hot-Pressed and Fired Samples [15]

Composition	Relative density, %	
	Hot-pressed samples	Fired samples
SiC–Y <sub>2</sub> O <sub>3</sub> –Yb <sub>2</sub> O <sub>3</sub>	96.5	94.3
SiC–Y <sub>2</sub> O <sub>3</sub> –Sm <sub>2</sub> O <sub>3</sub>	95.8	93.8
SiC–Yb <sub>2</sub> O <sub>3</sub> –Sm <sub>2</sub> O <sub>3</sub>	94.5	93.0

**TABLE 6.** Characteristics of Silicon Carbide Based Ceramic with Additives in the Systems AlN–M<sub>2</sub>O<sub>3</sub> [16]

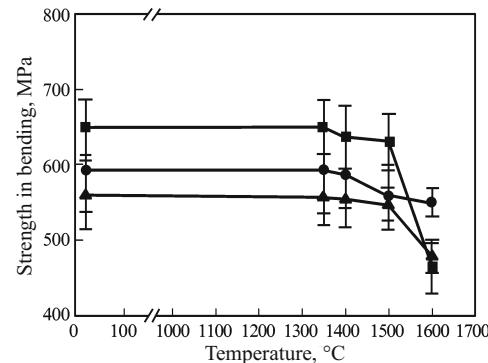
Additive	Batch components, wt.%	Relative density, %	Crystalline phase	
			primary	secondary
AlN–Y <sub>2</sub> O <sub>3</sub>	85.6 $\beta$ -SiC + 0.9 $\alpha$ -SiC + 2.9 AlN + 10.6 Y <sub>2</sub> O <sub>3</sub>	98.1	$\alpha$ -SiC	$\beta$ -SiC
AlN–Yb <sub>2</sub> O <sub>3</sub>	78.9 $\beta$ -SiC + 0.8 $\alpha$ -SiC + 2.7 AlN + 17.6 Yb <sub>2</sub> O <sub>3</sub>	98.6	$\alpha$ -SiC	$\beta$ -SiC
AlN–Er <sub>2</sub> O <sub>3</sub>	79.6 $\beta$ -SiC + 0.8 $\alpha$ -SiC + 2.7 AlN + 16.9 Er <sub>2</sub> O <sub>3</sub>	98.9	$\alpha$ -SiC	$\beta$ -SiC



**Fig. 6.** Microstructure of SiC-based ceramic with additives: a) AlN–Y<sub>2</sub>O<sub>3</sub> and b) AlN–Yb<sub>2</sub>O<sub>3</sub> [16].

paction by liquid-phase sintering. The microstructure of the materials is represented by elongated grains, smaller in the case of the yttrium oxide additive (Fig. 6) [16]. The results of a determination of the ultimate strength in bending are presented in Fig. 7.

The silicon carbide based ceramic with yttrium oxide as additive manifests constant strength (650 MPa) from room temperature to 1350°C. At 1400°C the strength in bending decreases to 630 MPa, which remains to 1500°C. The silicon carbide ceramic with ytterbium oxide additive is characterized by strength 550 MPa to 1500°C. At 1600°C the strength sharply decreases to 460 MPa, since the intergrain phase softens [16].



**Fig. 7.** Strength in bending versus temperature: ■) AlN–Y<sub>2</sub>O<sub>3</sub>; ●) AlN–Er<sub>2</sub>O<sub>3</sub>; ▲) AlN–Yb<sub>2</sub>O<sub>3</sub> [16].

Data on the high-temperature degradation of the properties of liquid-phase-sintered silicon carbide due to the presence of residues of the glassy phase are presented in many works [17 – 19]. It is shown that the intergrain glassy film has a positive effect on the low-temperature stability of the ceramic but limits the properties at temperatures above the softening point.

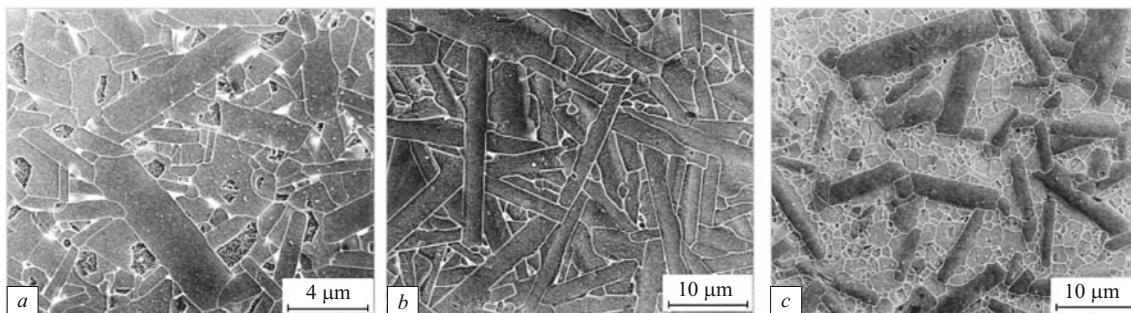
A method of obtaining a dense ceramic by hot-pressing β-SiC powder at 1880°C under pressure 30 MPa with Al<sub>2</sub>O<sub>3</sub>–Y<sub>2</sub>O<sub>3</sub> as the sintering additive is examined in [20]. The character of the sintering and the characteristics of the microstructure of the new material depended on the type and amount of the liquid phase formed as a result of the interaction of additives with SiO<sub>2</sub> present in the initial powders. The process of pressure-less oxidation of the liquid-phase-sintered SiC with sintering additives 5Al<sub>2</sub>O<sub>3</sub> + 3Re<sub>2</sub>O<sub>3</sub> (Re = La, Nd, Y, Er, Tm and Yb) was studied.

The bending strength of the samples at 20 and 1000°C was about 750 and 550 MPa, respectively. The observed decrease of the strength at 1300°C is due to the softening of the phase between the grains. For high-density materials the fracture toughness and hardness were 2.95 – 3.17 MPa · m<sup>0.5</sup> and 21 – 23 GPa, respectively.

An especially important characteristic of SiC-based materials obtained by liquid-phase sintering is the essential con-

**TABLE 7.** Batch Components and Process Conditions of Materials Based on Silicon Carbide [22]

Additive	Batch components, wt.%	Relative density, %	Process conditions							
			Hot pressure			Firing				
			Temper-ature, °C	Time, h	Pressure, MPa	Medium	Temper-ature, °C	Time, h	Pressure, MPa	Medium
SC1	77.98 β-SiC + 0.79 α-SiC + 11.40 AlN + 19.82 Er <sub>2</sub> O <sub>3</sub>	99.0	1900	1	25	N <sub>2</sub>	2000	6	25	N <sub>2</sub>
SC2	85.60 β-SiC + 0.90 α-SiC + 13.50 Y <sub>2</sub> Al <sub>5</sub> O <sub>12</sub>	98.9	1810	1	25	Ar	1910	6	25	Ar
SC3	86.64 β-SiC + 0.87 α-SiC + 7.05 Al <sub>2</sub> O <sub>3</sub> + 4.08 Y <sub>2</sub> O <sub>3</sub> + 1.36 CaO	98.5	1810	1	25	Ar	1910	4	25	Ar



**Fig. 8.** Microstructure of silicon carbide with additives: *a*) SC1, *b*) SC2, and *c*) SC3 [22].

tent (in their microstructure) of a secondary phase along grain boundaries and at triple points. The choice of sintering additives affects many properties which are important for use as a construction material. One of the leading properties is the resistance to oxidation as a result of the formation of silicon oxide at the contact boundary with an aggressive medium. Oxidation occurs not only by direct diffusion of oxygen into the interior volume with formation of  $\text{SiO}_2$  but also by back diffusion of metal cations from the intercrystallite phase and their subsequent reaction with part of the  $\text{SiO}_2$  formed [21].

Attention is given to the healing of cracks in a silicon-carbide ceramic obtained by liquid-phase sintering [22]. The heat-treatment temperature has a decisive effect on the degree to which strength is restored and the rate of healing of the cracks. After firing in air at the temperature with the authors of [22] call optimal, a crack vanishes almost completely and the strength is restored to the level of the initial samples. It was shown that simple heat-treatment of SiC ceramic sintered with  $\text{CaO}-\text{Y}_2\text{O}_3-\text{Al}_2\text{O}_3$  additive in air at 1100°C for 1 h even leads to a further increase of the strength to 1054 MPa.

In [22]  $\alpha$ -SiC,  $\beta$ -SiC, AlN,  $\text{Er}_2\text{O}_3$ ,  $\text{Y}_3\text{Al}_5\text{O}_{12}$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{Y}_2\text{O}_3$  and CaO (99.9% purity) were used as the initial powders. The average particle sizes of the  $\alpha$ -SiC and  $\beta$ -SiC powders were 0.45 and 0.29  $\mu\text{m}$ , respectively, and the specific surface areas of the powders were 15 and 17.5  $\text{m}^2/\text{g}$ , respectively. The treatment regimes of the materials are presented in Table 7, and the batch compositions are also indicated.

The heat-treatment time in air was 1 h in the temperature interval from 1200°C to 1500°C for the material SC1, 1100 to 1300°C for the ceramic SC2 and 1000 to 1200°C for the composition SC3.

**TABLE 8.** Fracture Strength and Strength in Bending [22]

Material	Ultimate strength in bending, MPa	Fracture toughness, $\text{MPa} \cdot \text{m}^{1/2}$
SC1	$717 \pm 46$	$5.9 \pm 0.45$
SC2	$636 \pm 12$	$8.0 \pm 0.52$
SC3	$721 \pm 35$	$7.0 \pm 0.47$

Figure 8 illustrates the effect of the crack healing process on the strength of the three materials studied. The ceramics SC1 and SC2 are represented by plate-shaped grains of  $\alpha$ -SiC; x-ray structural analysis attests to the presence of a phase transition  $\beta$ -SiC  $\rightarrow$   $\alpha$ -SiC occurring during firing. The material SC3 is represented by a set of plate-shaped grains of  $\alpha$ -SiC and equiaxial grains of the matrix. The values of the fracture toughness and strength in bending at room temperature of the materials SC1, SC2 and SC3 are presented in Table 8.

In summary, it can be stated with confidence that liquid-phase sintering of silicon carbide ceramic with the participation of eutectic additives is promising for obtaining materials with high physical and mechanical properties combined with lower energy, resource and materials consumption. In the not too distant future silicon carbide ceramic will be able to replace heat-resistant alloys operating at very low temperatures.

In addition, the use of silicon carbide ceramic synthesized by liquid-phase sintering as armor materials will make it possible to raise the armor-protection class compared with the known types of ceramic armor with the same thickness. This is certain to open up wide prospects for it.

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